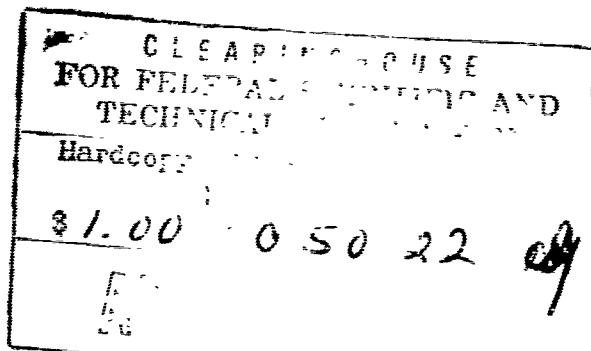


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CARBORANE - SILOXANE ELASTOMERS

Report Period: 19 May 1965 through 18 August 1965



Thiokol
CHEMICAL CORPORATION
REACTION MOTORS DIVISION
DENVILLE NEW JERSEY



CARBORANE-SILOXANE ELASTOMERS

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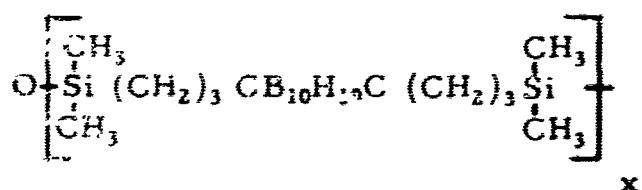
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FOREWORD

This report was prepared by Thiokol Chemical Corporation, Reaction Motors Division, under U. S. Army Contract No. DA-11-070-AMC-852(W). It covers work done in the second quarter of the program during the period 19 May 1965 through 18 August 1965. Mr. Z. T. Ossefort of Rock Island Arsenal, Illinois is the Project Engineer. Contributors at Thiokol are, Mr. Nathan Mayes (Principal Scientist) and Mr. Alan Jackson.

ABSTRACT

Investigation of carborane-siloxane polymer synthesis was continued. Polymeric products with the structure



were prepared by silylalkoxy-silylhalide condensation polymerization, hydrolysis condensation polymerization of silylhalides, and by ring-opening polymerization of a cyclosiloxane. Thermal stability of carborane-siloxane polymers was determined by thermogravimetry and molecular weight changes in heat treated materials.

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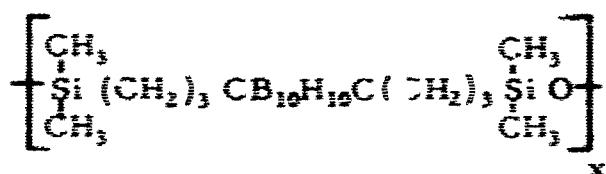
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I. INTRODUCTION

The objective of this program is the synthesis of thermally stable carborane siloxane elastomers. Carborane siloxane polymers have been prepared previously which contained carborane either in the backbone or as pendant groups (Ref 1 and 2). These polymers were thermally stable to temperatures above 400°C as shown by TGA. They were also elastomeric when the carborane units, either backbone or pendant, were sufficiently spaced to permit chain flexibility. The structures with pendant carborane groups had backbones that were wholly or primarily repeating siloxane groups and as such are capable of undergoing thermal rearrangement to form stable siloxate cyclic compounds. Moreover, the previously prepared backbone carborane siloxane polymers were potentially hydrolytically unstable due to the presence of silico-carborane linkages which in analogous monomeric compounds have been shown to be readily hydrolyzed.

The choice of structures to be investigated on this program was influenced by the foregoing considerations and as a result the structure that was considered to be most favorable for the objective was:



It was anticipated that there would be no silicon-carborane bonds to be hydrolyzed, that repeating siloxane linkages that could decompose through cyclic siloxane formation would be minimized and that the polymethylene and siloxane groups in the backbone would give flexible chains.

The program was initiated with the preparation of silane, carborane, and carborane-silane compounds for use in the preparation of polymers with structures of the desired type. Among the materials prepared were: (1) chlorodimethylsilane, (2) tetramethyldisiloxane, (3) 1,7-diallyl-*m*-carborane, and (4) 1,7-bis[*n*-chlorodimethylsilyl]propyl-*m*-carborane.

Polymerization studies were begun and several methods of obtaining the desired polymer structure were investigated. These included silylhydride-addition

polymerization, alkoxy silane-halo silane condensation polymerization and hydrolysis condensation polymerization. The silylhydride-addition polymerization which involved the catalyzed reaction of tetramethyl disiloxane with 1,7-diallyl-m-carborane yielded low molecular weight products. On the basis of these results and the inability of a number of other investigators (Ref 3, 4 and 5) to achieve high molecular weight products from silylhydride-addition polymerization, this avenue of investigation has been abandoned. The other polymerization methods appeared more promising and their investigation was continued. One of the products obtained from the hydrolysis condensation polymerization of 1,7-bis[3-(chlorodimethylsilyl)propyl]m-carborane was particularly interesting since it appeared to be a m-carborane cyclosiloxane that might be capable of ring-opening polymerization. As a result, most of the synthesis work of the second quarter of the program has been concerned with the preparation, characterization and polymerization of this suspected m-carborane cyclosiloxane. In addition, a new carborane-siloxane monomer was prepared, investigation of alkoxy silane-halo silane polymerization was continued, and characterization of carborane-siloxane polymer thermal and thermal-oxidative stability was initiated.

II. TECHNICAL PROGRESS

PHASE I - MONOMER AND POLYMER SYNTHESIS

A. Carborane Intermediates and Monomers

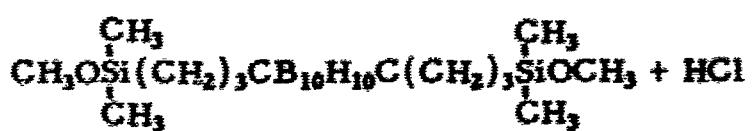
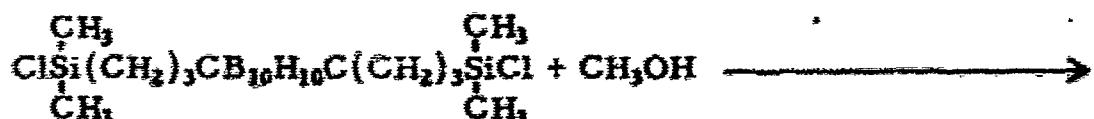
1. 1,7-Bis[3-(chlorodimethylsilyl)propyl]-m-carborane.

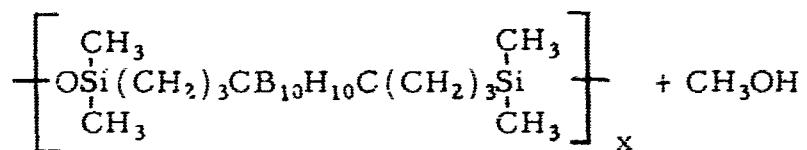
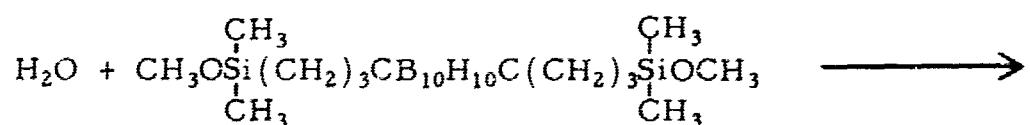
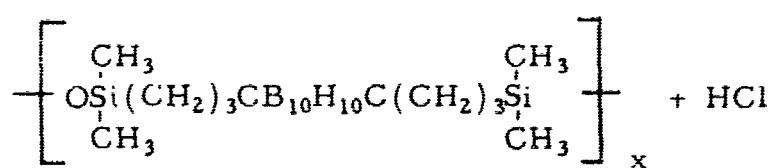
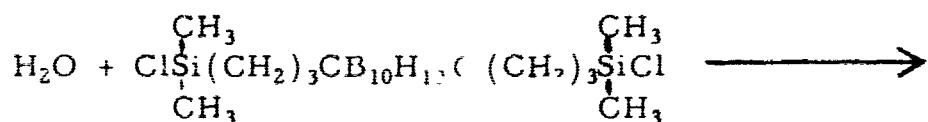
Elemental analyses together with infrared and n.m.r. analyses have confirmed the structure of 1,7-bis[3-(chlorodimethylsilyl)propyl]-m-carborane prepared by addition of two moles of chlorodimethylsilane to one mole of 1,7-diallyl-m-carborane (Ref 6).

Calculated for $C_{12}H_{34}B_{10}Cl_2Si_2$: C, 34.84; H, 8.29; B, 26.16; Cl, 17.83; N.E. 206.8 Found: C, 34.18; H, 8.85; B, 25.94; Cl, 17.17; N.E. 209.8.

2. 1,7-Bis[3-(methoxydimethylsilyl)propyl]-m-carborane

The preparation of 1,7-bis[3-(methoxydimethylsilyl)propyl]-m-carborane was attempted by the reaction of 1,7-bis[3-(chlorodimethylsilyl)propyl]-m-carborane with excess methanol after the analogous procedure to prepare 1,7-bis(methoxydimethylsilyl)-m-carborane (Ref 7). Our efforts produced siloxanes that apparently resulted from reaction of the chlorosilane or intermediate methoxysilane with water formed from reaction of hydrogen chloride and methanol (Ref 8).

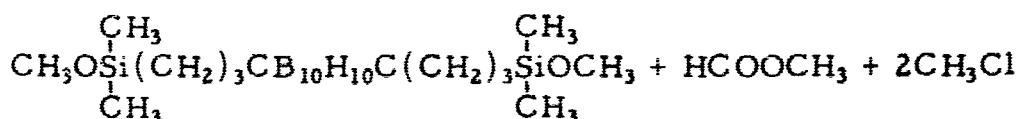
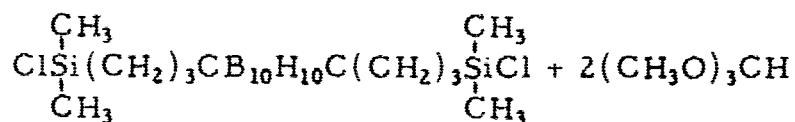




Modification of the reaction conditions to use methyl orthoformate instead of methanol resulted in the preparation of 1,7-bis[3-methoxydimethylpropyl]-m-carborane which was obtained as a colorless liquid of bp 142-150° at 0.02 mm.

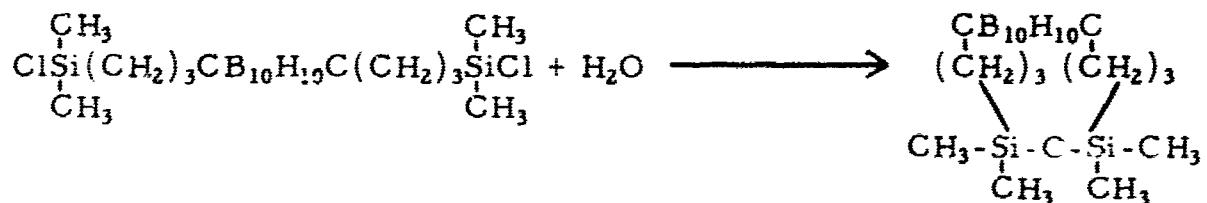
Calculated for $\text{C}_{14}\text{H}_{40}\text{B}_{10}\text{Si}_2\text{O}_2$: C, 41.54; H, 9.96; B, 26.71; Si, 13.88.

... C: C, 41.00; H, 10.73; B, 26.4; Si, 11.11

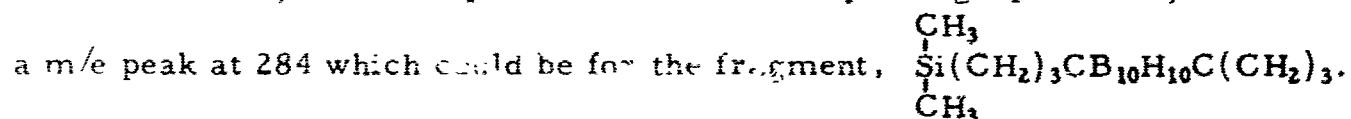


3. α -Oxa-2, 12-disila-2, 2, 12, 12, -tetramethyl-6, 7, 8-(1, 7-m-carboranylene -cyclododecane

Hydrolysis of 1, 7-bis[3-(chlorodimethylsilyl)propyl]-m-carborane yielded a crystalline product which is apparently a 12-membered m-carborane exocycle.



The crystalline product was obtained in small yield (<10%) on bulk hydrolysis of the silane; however, yields were increased to 45% upon use of acetone as solvent. The remaining portion of hydrolysis product was linear polymer. The crystalline material was isolated by sublimation at 180-230°C/0.04 mm Hg. The sublimed product was recrystallized from acetone-chloroform to yield white needle crystals of mp 176.5°C. A mass spectrographic analysis showed



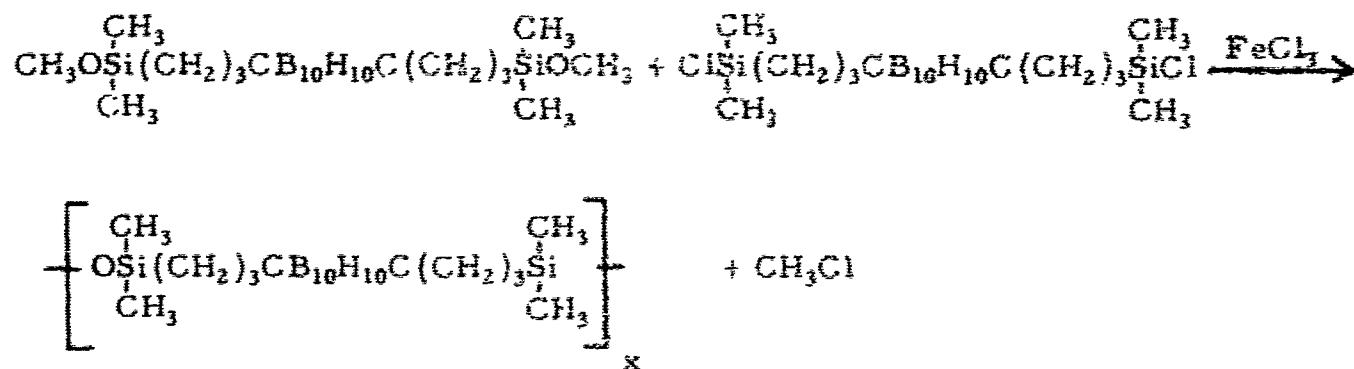
No parent peak was noted. Infrared analysis supports the proposed structure with absorption peaks at 2930 cm^{-1} for the C_2H_2 , at 2600 cm^{-1} for BH , at 1250 cm^{-1} for SiCH_3 , at 1175 cm^{-1} for $\text{Si}(\text{CH}_2)_3\text{CB}_{10}\text{H}_{10}\text{C}$, and at 1052 cm^{-1} for $\text{Si}-\text{O}-\text{Si}$. A molecular weight determination by the cryoscopic method supported the proposed structure. An n.m.r. analysis yielded an extremely complex spectrum which did not prove or disprove the structure. An elemental analysis did not support the structure; however, this analysis will be repeated.

Calculated for $\text{C}_{12}\text{H}_{34}\text{B}_{10}\text{OSi}_2$: C, 40.18; H, 9.55; B, 30.14; Si, 15.66; mol. wt. 358; Found: C, 42.64; H, 10.58; B, 27.66; Si, 12.21; mol. wt. 377.

B. POLYMERS

1. Alkoxysilane-Halosilane Condensation Polymerization

Previous efforts on this program to prepare carborane-siloxane polymer by the ferric chloride catalyzed condensation of diethoxydimethylsilane with 1,7-bis[3-(chlorodimethylsilyl)propyl]-m-carborane yielded a low molecular weight liquid polymer (Ref 6). A similar polymerization was recently reported to give high molecular weight polymer by allowing 1,7-bis(methoxydimethylsilyl)-m-carborane to react with 1,7-bis(chlorodimethylsilyl)-m-carborane at temperatures up to 230°C with ferric chloride catalyst (Ref 9). This procedure was used on this program to polymerize 1,7-bis[3-(methoxydimethylsilyl)propyl]-m-carborane and 1,7-bis[3-(chlorodimethylsilyl)propyl]-m-carborane.



In this case, however, although the reaction was conducted at temperatures up to 230°C and the ferric chloride catalyst was added incrementally, relatively low molecular weight product resulted as determined by inspection of the product and by the fact that only 70% of the theoretical quantity of methyl chloride was collected. The product was a dark colored viscous liquid. The color, which was apparently due to the ferric chloride, could not be removed by washing with water, acetone or chloroform. This type reaction does not appear to be suitable for the preparation of high molecular weight products of the type being sought here.

2. Hydrolysis/Condensation Polymerization

The polymeric product obtained by hydrolysis of 1,7-bis[3-(chlorodimethylsilyl)propyl]-m-carborane from which low molecular weight product had been removed by sublimation (Ref 6) had a molecular weight of 5200 as

determined by vapor pressure osmometry. An attempt to increase the molecular weight by treating the polymer with sulfuric acid was not successful.

3. Ring-Opening Polymerization

The compound proposed to be 1-oxa-2,12,-disila-2,2,12,12-tetramethyl-6,7,8-(1,7-m-carboranylene)cyclododecane was converted to polymer by the action of sulfuric acid and heat. The crystalline compound was mixed in the bulk state with 2 mole percent concentrated sulfuric acid and heated above the melting temperature at 185°C. A reaction occurred immediately to give an increasingly viscous reaction mass. After being heated for one hour and cooled to room temperature the product was an elastomeric gum. The gum was completely soluble at low concentrations in aromatic solvents such as benzene and toluene. The sulfuric acid catalyst was removed from the gum by washing a toluene solution with water.

A small amount of unreacted starting material remained in the gum and was removed by sublimation at 200°/0.04 mm Hg. Such incomplete conversion to polymer is typical of cyclosiloxane ring-opening polymerization. The conversion of dimethylcyclosiloxanes to linear polymer does not exceed 90%. The product always contains about 10% of the starting siloxanes (Ref 10).

The gum produced by ring-opening was very similar in physical properties to the gum produced by hydrolysis/condensation. The latter material had a molecular weight of about 5000 and it may be assumed that the ring-opening product was of similar molecular weight. It is expected that the molecular weight obtained by ring-opening may be increased significantly by regulating the catalyst concentration. It has been shown that polymerization of octamethylcyclotetrasiloxane using concentrated sulfuric acid catalyst yielded product of 10,000 molecular weight; however, upon dilution of the reaction mixture with water the molecular weight increased to 70,000. Similar procedures as well as investigation of other acid and base catalysts will be investigated for the carborane-siloxane ring-opening polymerization.

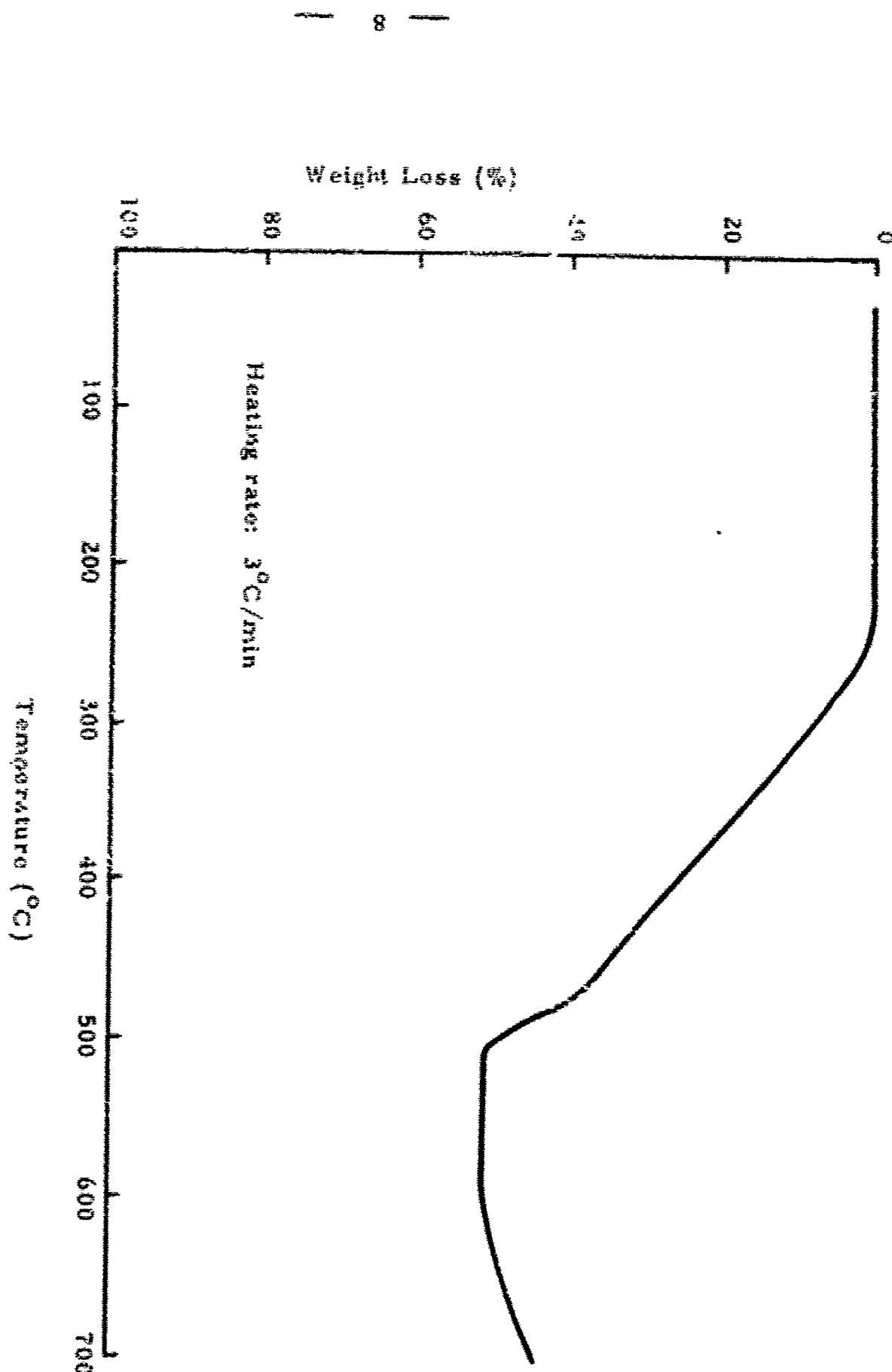
PHASE II - EVALUATION OF POLYMERS FOR THERMAL STABILITY

Initial thermal evaluation of the polymer obtained by hydrolysis of 1,7-bis[3-(chlorodimethylsilyl)propyl]-m-carborane was done by TGA in air and nitrogen atmospheres (Figures 1 and 2). Oxidative thermal degradation commenced at 240°C and continued with weight loss to about 500°C. At 600°C a weight gain occurred which is undoubtedly due to the oxidation of carborane to

Figure 1.

TGA of $\left[\text{CH}_3\text{O}\text{Si}(\text{CH}_3)_2\text{C}_2\text{H}_5\text{OC}(\text{CH}_3)_2\text{Si}(\text{CH}_3)_2\right]_x$

In Air



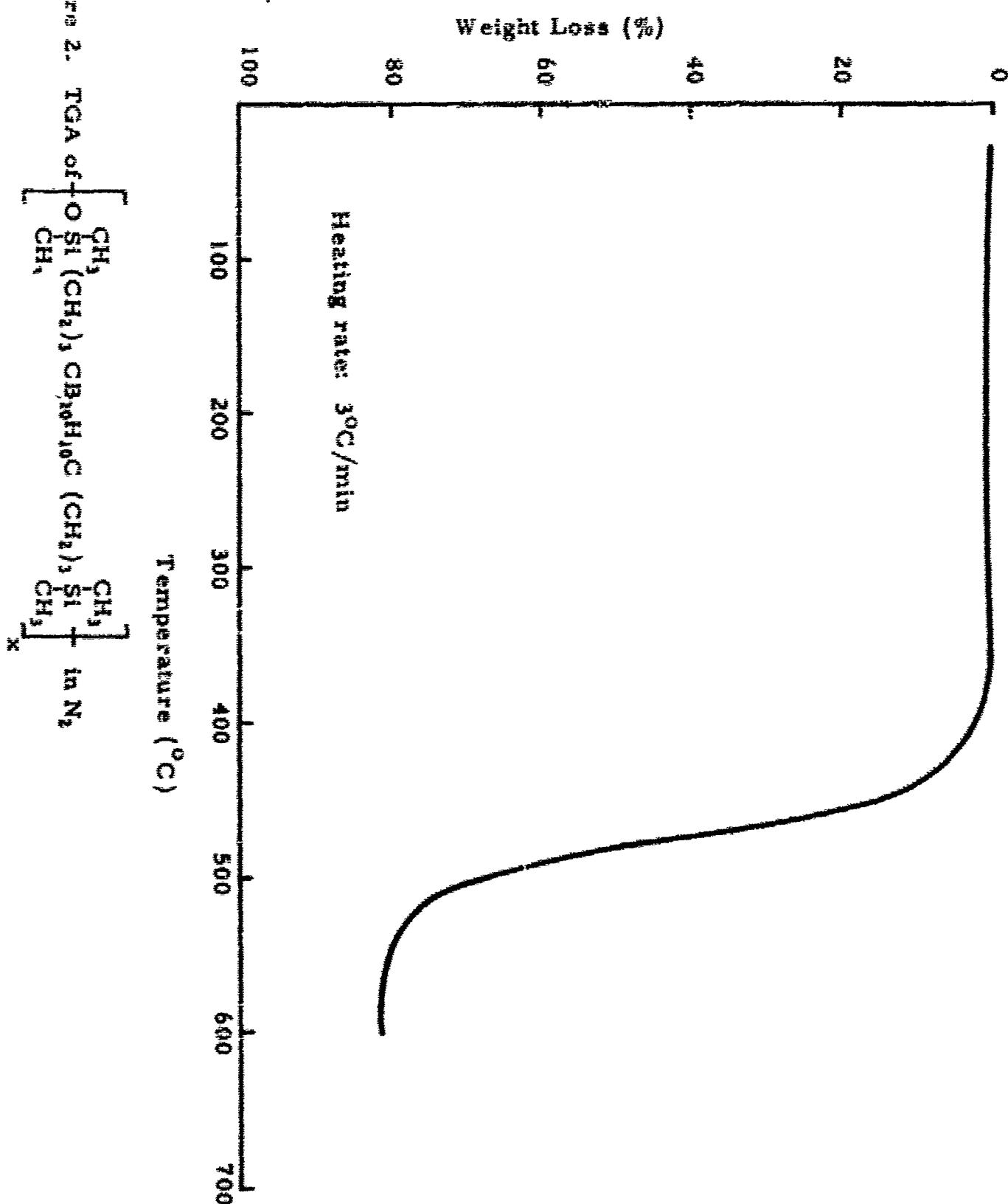
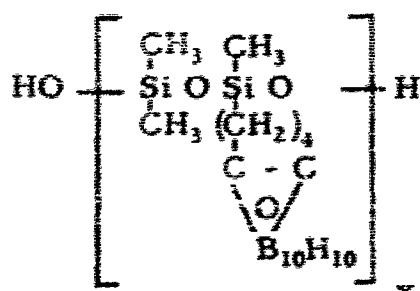


Figure 2. TGA of $\left[\text{O} \text{Si} \left(\text{CH}_3 \right)_2 \text{CH}_2 \text{H}_2\text{C} \left(\text{CH}_3 \right)_2 \text{Si} \left(\text{CH}_3 \right)_2 \right]_x$ in N_2

form nonvolatile boron oxides. The oxidative process which started at 240°C is at least partly the oxidation and splitting off of methyl groups. This process occurs in polydimethylsiloxanes to a small degree at 200°C and to considerable extent at 250°C (Ref 11). The oxidative degradation must also include another process since maximum weight loss due to methyl groups could be only 17%. The weight loss actually observed up to 370°C is 20%. Beyond 370°C thermal degradation is also in progress as indicated in Figure 2. The additional oxidative process probably involves scission of Si-C bonds in the polymer backbone to give volatile fragments.

Thermal degradation in the carborane-siloxane polymer is not analogous to thermal degradation in polydimethylsiloxane. The latter polymer thermally degrades by rupture of Si-O bonds starting at 300°C and becoming very intense at 400°C (Ref 12). Thermal degradation of the carborane-siloxane polymer starts at about 370°C and becomes intense above 400°C. The driving force for the rupture of Si-O bonds of polydimethylsiloxane is the formation of cyclic siloxanes. Such cyclic formation is enhanced by the arrangement of the chains in a helical conformation having 3-6 silicon atoms in a single turn of the helix. This structure favors chain rupture with resulting ring closure at high temperatures. The carborane-siloxane polymer having only one S-O bond per twelve chain atoms would have to form a helical structure of exactly twelve atoms per turn in order to decompose analogously to polydimethylsiloxane. This is an extremely unlikely occurrence.

TGA is a valuable tool for screening the thermal stability of materials; however, it has limitations. The carborane-siloxane polymer that appears to be thermally stable to 370°C may be degrading at a lower temperature but not forming volatile fragments. A method of determining such behavior is the measurement of polymer molecular weight changes that occur on heating. This study was initiated by investigating the thermal stability of a carborane-siloxane polymer of the structure



This polymer which has previously shown thermal stability to over 400°C by TGA has now been shown to undergo competing processes of polymerization and depolymerization at high temperatures. Polymerization occurs through condensation of hydroxy terminals and depolymerization is by cyclic formation as in polydimethylsiloxane. The data, presented in Table I, show that thermal reaction occurred at each temperature studied. At 180°C the reaction was exclusively or predominantly polymerization as indicated by the increase in molecular weight; however, at 200°C and 250°C smaller increases in molecular weight indicate that depolymerization must also have occurred. At 300°C depolymerization resulted in a net decrease in molecular weight. Thus the rate of depolymerization increased with temperature and presumably continued until the equilibrium molecular weight was reached.

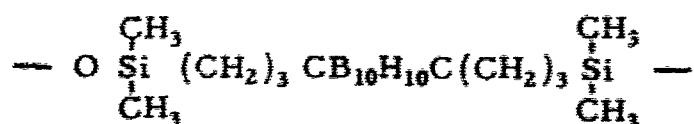
A similar study will be conducted with the carborane-siloxane polymer containing carborane in the backbone. It is anticipated that this material will have substantially higher thermal stability due to its structure which discourages cyclic formation.

TABLE I
THERMAL STABILITY OF PENDANT
CARBORANE SILOXANE POLYMER

Temperature, °C	Time, hr	Molecular Weight	
		Original	After Heating
180	40	4500	8300
200	40	4500	5500
250	40	4500	4800
300	40	4500	4000
300	24	7700	4600
300	168	7700	1580
350	24	7700	2600

III. SUMMARY

This is a program to synthesize thermally stable carborane-siloxane elastomers. The polymer structure being investigated for this objective is one having the grouping

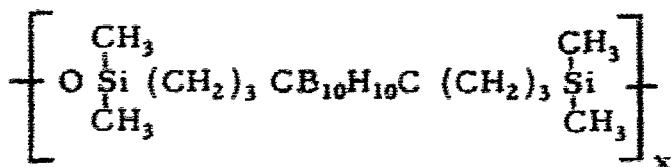


in the chain backbone. In previous work on this program silane and carborane intermediates were prepared and polymerization studies were initiated. Of the methods of polymerization studied, polymerization by catalyzed addition of disilylhydrides to diolefins has been abandoned as impractical for obtaining high molecular weight products.

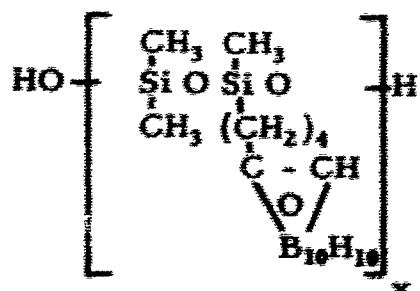
The continued investigation has included polymerization of silylhalide and silylalkoxy derivatives by ferric chloride catalyzed condensation. This necessitated the preparation of a new carborane-silane intermediate, 1,7-bis[β -('methoxycdimethylsilyl)propyl]- m -carborane. The alkoxy-halide polymerization yielded low molecular weight product.

Hydrolysis-condensation polymerization of 1,7-bis[β , chlorodimethyl silyl)propyl]- m -carborane yielded linear siloxane polymer of 5200 molecular weight and a crystalline material believed to be 1-oxa-2,12-disila-2,2,12,12-tetramethyl-6,7,8-(1,7- m -carboranylene)cyclododecane. Polymerization of this cyclic compound was effected with sulfuric acid catalyst to give polymer of about 5000 molecular weight.

Studies to characterize carborane-siloxane polymers for thermal and thermal oxidative stability were initiated. Thermogravimetric analysis indicated that polymer of the structure



underwent thermal oxidation and weight loss starting at 240°C (about the same temperature as for polydimethylsiloxane). Weight loss due to thermal degradation in the absence of oxygen started at 370°C. A study was initiated to determine the temperature of thermal rearrangements in carborane-siloxane polymers that are not manifested by weight changes but are indicated by molecular weight changes. Results obtained to date on polymers of the structure



show this material to undergo both polymerization and depolymerization at elevated temperatures with depolymerization becoming the dominant process above 250°C. The ease with which this polymer thermally rearranges is attributed to its ability to form cyclics analogous to polydimethylsiloxane. Greater thermal stability is anticipated for the polymer containing carborane in the backbone due to its relative inability to form cyclic degradation products.

IV. REFERENCES

1. Olin Mathieson Chemical Corporation, Monthly S. R., No. 34, Contract NOnr 3395(00), Project No. 356-431, December 1963.
2. Thiokol Chemical Corporation, Reaction Motors Division, Report RMD 5038-F, Contract NObs 90065, April 1964.
3. Rock Island Arsenal Laboratory, Report No. 62-4162, Department of the Army, Project No. 599-25-001, Ordnance Management Structure Code No. 5010.11. 838, December 1962.
4. Ibid. Report No. 64-2899, Department of the Army Project No. IC014501B13A, AMC Code No. 5011. 11. 852, October 1964.
5. Yarsley Research Laboratories Ltd., Contract No. DA-91-591-EUC-2482, Ref No. E.8669/4/15, June 1963.
6. Thiokol Chemical Corporation, Reaction Motors Division, Report RMD 5065-Q1, Contract No. DA-11-070-AMC-852(W), May 1965.
7. S. Papetti and T. L. Heying, *Inorg. Chem.* 3, 1448 (1964).
8. C. Raboro, Organosilicon Compounds, Butterworths Scientific Publications, London (1960), p. 289.
9. S. Papetti, B. B. Schaeffer, A. P. Gray and T. L. Heying, Olin Mathieson Chemical Corporation, Technical Report No. 26, June 1965.
10. K. A. Andrianov, Metalorganic Polymers, Interscience Publishers, New York (1965), p. 220.
11. Ibid., p. 55; F. G. A. Stone and W. A. G. Graham, Inorganic Polymers, Academic Press, New York (1962), p. 255.
12. K. A. Andrianov, Metalorganic Polymers, Interscience Publishers, New York (1965), p. 60.